Fundamentals of Spectroscopy
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Lecture-20
Polyatomic Molecules II and Numericals

Hello everyone in the last lecture we discussed about polyatomic molecules. Today we will start with calculating the moment of inertia of water.

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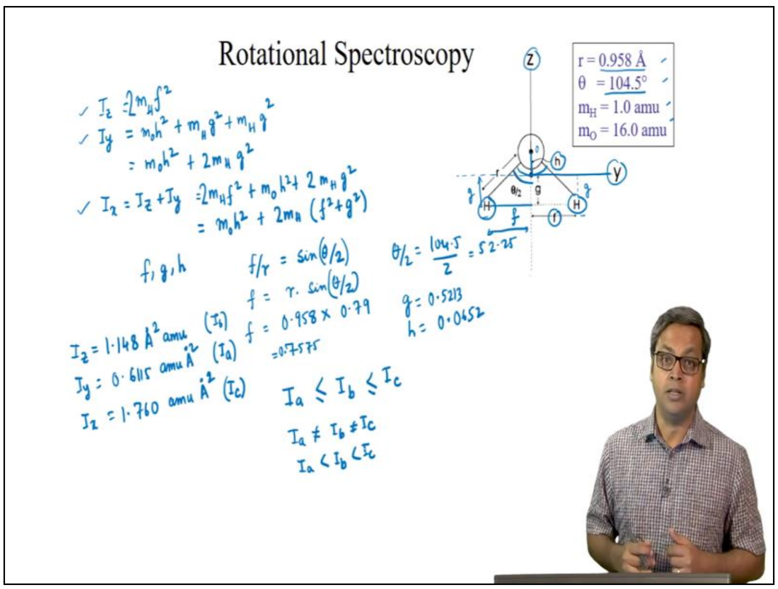

So, water as we know is a planar molecule with all the atoms that is the 2 hydrogen atoms and the oxygen atom they are all in one plane. So, here we have the water molecule, so this is the oxygen atom and these are the 2 hydrogen atoms and here we see the z axis and the y axis the x axis is out of the plane of the water molecule that means if this is the water molecule then the x axis is out of the plane of the water molecule.

Now we can calculate the moment of inertia along the different axis. So, let us start with the z axis so we will calculate I z so because the oxygen atom lies along the z axis so it will not contribute to the moment of inertia along the z axis, so the only the 2 hydrogen atoms will contribute. So, I can write I z so the contribution from the hydrogen atom is the mass of hydrogen and then the perpendicular distance from the hydrogen atom to the z axis we can see this is given by F.

So, I can write m H f squared, now if you want to do it for the y axis so we can write I y equals now you see the center of mass does not lie or the oxygen atom does not coincide with the center of mass. So, the oxygen atom will also contribute to I y, so we will have the mass of oxygen times we have H here that is the distance between the oxygen atom and the center of mass that is m oxygen H squared then we have the mass of hydrogen and as you can see this hydrogen is g distance away from the y-axis so the mass of hydrogen times g squared.

Also the other hydrogen atom is g distance away so we have another term another mass of hydrogen terms times g squared so we can write this as m 0 H squared + 2m H g squared. So, for any planar molecule the out-of-plane moment of inertia is equal to the sum of the 2 in-plane moments of inertia. So, because the outer plane moment of inertia here is I x, we can write I x equals I z + I y so we can write this as m H f squared + m oxygen H squared + 2m hydrogen g squared.

So in I z I made a mistake so it should be 2 times mass of hydrogen because there are 2 hydrogen atoms, so it should be 2 here so what we have is m oxygen H squared + 2 mass of hydrogen f squared + g squared. So, now let us use the real values. So, the real value that is the internalized distance the OAH bond length is 0.985 angstrom and the angle between the hydrogen oxygen hydrogen that H O H angle that is given where theta equals 104.5 degrees and the mass of hydrogen of the mass of oxygen are one and 16 atomic mass unit.

So, we need to calculate if we know all these numbers from these numbers we need to calculate the values of f, g and H. so, let us see first the value of f so as we can see this distance is f and this angle is theta by 2 so we can write that f by r equals sine theta by 2, so f I can write r times sine theta by 2 now theta by 2 equals 104.5 by 2 that is 52.25 so what we can write here we can write f equals 0.958 times sine of 52.25.

If you do that you get 0.79 so the value of f becomes 0.7575 so if we do the similar math we get g equals 0.5213 and H equals 0.0652 so if we put the values of f, g and H back into the expression of I z I y and I x what we get we get is I z equals 1.148 angstrom squared a mu I y equals 0.6115 we can write this a mu angstrom squared and I x becomes 1.760 a mu angstrom squared. So, now if we think in terms of a b and c axis that is a principal axis of inertia, so we can see that because here I x has the largest value so this will be our c axis.

So, this will be I z, I y has the lowest value so that will be our I a and I z will be I b, this is because we have discussed before that I a is less than I b is less than I c. So, we can see that the moments of inertia are all different in the 3 different directions. So, because in this case I a not equal to I b not equal to I c and also I a is less than I b is less than I c we can say water is an asymmetric rotor and we had already discussed this or mentioned this in the last lecture.

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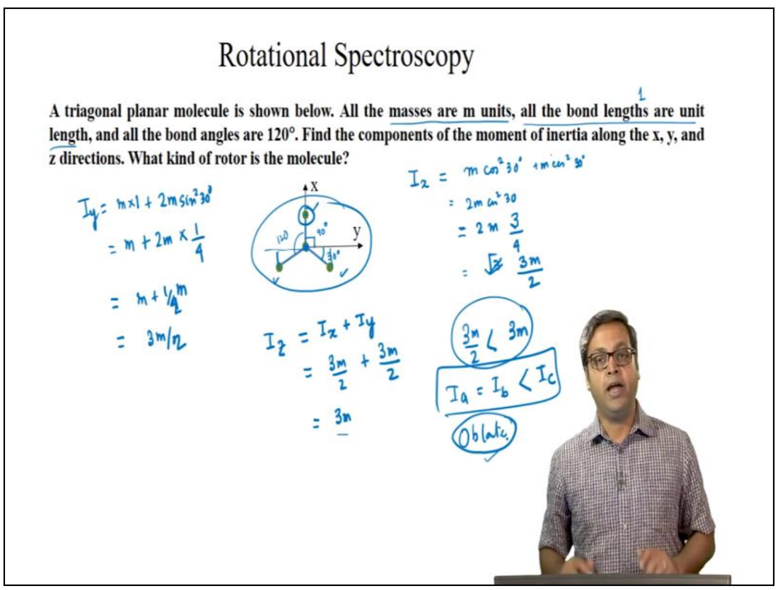

So, now let us look into another similar problem. So. here we have our trigonal molecule which is shown below so all the masses are m units so there are 4 atoms and all the 4 atoms or masses of m. And all the bond lengths are of unit length that means the bond length is 1 and all the bond angles are 120 degree. So, we have to find the components of the moment of inertia along the x, y and z directions. And we have to also find what kind of rotor is this molecule. So, because this is 120 and this angle is 90 degrees so we know that this angle is 30 degrees.

So, first we will find the moment of inertia along x axis and because these 2 atoms around the x axis these 2 atoms would not contribute. So, what we have is m times cos square 30 degrees + m times cos square 30 degrees. So, that is 2 m cos square 30 so that is 2 times m times 3 by 4 so that becomes root 3 or sorry this is 3 m by 2, so now we find I y the I y this atom would not contribute because it is sitting on the center of mass but all the other 3 atoms will contribute.

So, contribution of this atom will be m times distance squared that is one and then we have 2 m sine square 30 degrees because then we are talking about the distance here. So, what we find is m + 2m times 1 by 4 that becomes m + 1/2 or m + m by 2 that is 3 m by 2. So, now we also need to find I z and because this molecule is in a plane so because of this planar molecule we can write as e equals I x + I y as we discussed in the last problem so that is 3 m by 2 + 3 m by 2 so what we have is 3m. So, I x equals 3m by 2 I y equals 3m by 2 and I is equals 3 m so we can see that because 3m by 2 is less than 3m so we can say that what we have here is I a equals I b less than I c.

So this is an oblate molecule or this is like a disc-shaped molecule. So, this molecule is a symmetric rotor of the oblate type. So, this brings us to the end of the discussion on rotational spectroscopy. Let us once revise what we have discussed so far we have started by looking into the correspondence between linear and angular motion.

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We introduced the concept of angular velocity that is Omega an angular momentum that is L and we saw that for a polyatomic molecule the moment of inertia I is given by summation i mi ri squared. So, we started discussing rotational spectroscopy with diatomic rigid rotors. We saw that the primary condition for obtaining a rotational spectrum is that the diatomic molecule should have a permanent dipole moment.

Does homo-nuclear diatomic molecules are micro as inactive because they have no permanent dipole moment but hetero-nuclear diatomic molecules are micro active. The energy of a rotating system is given by L square by 2 I where the angular momentum L is quantized and is given by root over J times J + 1 h cross where h cross equals h by 2 pi, so the energy of the Jth level is given by EJ that is h squared by 8 pi square I J times J + 1, the unit here is in joules.

So if we want to find the energy in wave number unit then we have nu bar J that is EJ by hc so we get h by 8 pi square I see J times J + 1 and we saw we can also write this as B times J times J + 1 where B is the rotational constant. So, we then looked into the selection rules for rotational spectroscopy and found that this election rule for the changes in the rotational quantum number J is Delta J equals + - 1. From this condition we saw that the delta nu bar J is given by 2B times J + 1 for a transition between from J to J + 1.

So this tells us that the lines in the rotational spectrum will be equally spaced right 2B thus B can be obtained directly from the rotational spectrum. As B is inversely proportional to the moment of inertia so B is inversely proportional to the moment of inertia and moment of inertia is given by mu r squared where mu is a reduced mass and r is the bond length or the internuclear distance. So, bond length or internuclear distance can be obtained directly from that rotational spectrum.

So then we discuss the isotope effect and we saw that the natural abundance can directly be obtained from the rotational spectrum. We then looked into the degeneracy of the rotational levels and introduced another quantum number mJ. For any J mJ can take 2 J + 1 values. So, each energy level is 2 J + 1 fold degenerate. In general the rotational energy is independent of mJ but in the presence of an external field the degeneracy is lifted another selection rule that is Delta mJ equals 0 or + i 1 becomes important.

We also discussed about the intensities of the rotational lines we saw that J max that is the J level with a maximum population is given by J max equals root over KT by 2B h C – half. So, in order to find the J level with the maximum population we have to choose the nearest integer of J max we then moved on to non rigid rotors and discussed the effect of centrifugal Distortion. The knowledge of the distortion constant that is D provides us a rough estimate of the vibrational frequency nu bar.

And finally we looked into polyatomic molecules the spherical rotor the symmetric rotor the prolate and the oblates and the asymmetric water. So, in the next lecture my co-instructor Anirban Hazra will tell you more about the rotational wave functions and the selection rules. We will end today's lecture by solving a few more problems.

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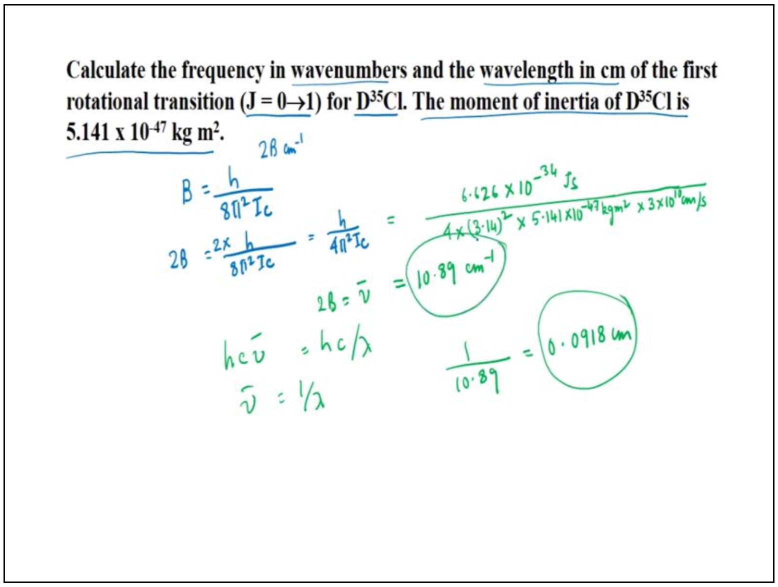

So, here we have the first problem. So, we have to calculate the frequency in wave numbers as well as the wavelength in centimeter of the first rotational transition that is J equals 0 to 1 for D 35CL. The moment of inertia of D 35CL is given by 5.141 times 10 to the power - 47 kilogram meter squared. So, we know the first transition comes out 2B wave numbers. We also know that B equals h by 8 pi square I c so we can write to be equals h by 8 pi squared I c times 2 that is h by 4 PI squared I c.

So now if we put the values so we have h that is 6.626 times 10 to the power - 34 Joule seconds then we have 4 times 3.14 squared times the moment of inertia that is 5.141 times 10 to the power - 47 kilogram meter squared and then we have the speed of light that is 3 times 10 to the power 10 centimeter per second. So, if we do this calculation we will get nu bar or 2B equals 10.89 wave numbers and we know that hc nu bar equals hc by lambda or nu bar equals 1 by lambda so we can write the wavelength is 1 by 10.89 that is 0.0918 centimeter.

So this is the wavelength and centimeter and this is the frequency in wave numbers for the first rotational transition of D 35CL.

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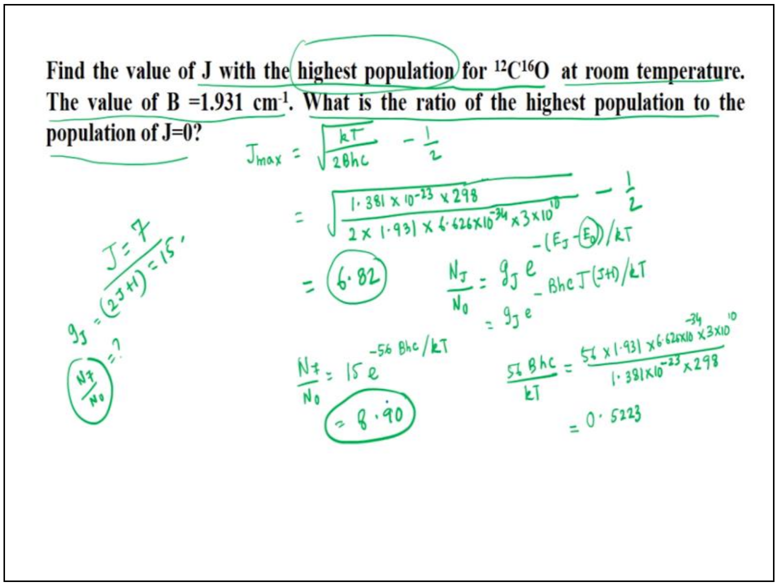

So, let us look into the next problem. So, in the next problem we have to find the J with the highest population for this carbon monoxide 12 C 16 O at room temperature. The value of B is given as 1.931 centimeter inverse. So, there is another question that is what is the ratio of the highest population to the population of J equals 0, so because we are talking about highest population we have to use the formula for J max, so J max equals root over KT divided by 2 B h c – half, so if we put the values here K is Boltzmann constant so this is 1.381 times 10 to the power - 23 times T, so this room temperatures will put 298 that is 25 degree Celsius.

And we have 2 times B is given as 1.931 and h that is 6.66 times 10 to the power - 34 and see that is 3 times 10 to the power 10. So, if we do this calculation and we have minus half here. So, the answer to this is 6.82, so we have to get the nearest integer so the nearest integer of 6.82 so the J level with highest population is J equals 7. So, now we have to find the ratio of the highest population to the population at J equals 0.

In other words because J equals 7 the degeneracy gJ equals 2J + 1 that is 15 so we have to find n 7 by n 0, so, we know that nJ by n 0 is given by gJ e to the power - EJ - e 0 by KT. So, E 0 we know is 0 and if we express in terms of B we have can write gJ e to the power - B h c times J times J + 1 divided by K T, so here J equals 7 so n 7 by n 0 that is given by g J that is 15 times e to the power - 7 times 8 that is J times J + 1 that is 56 B hc divided by KT.

So 56 B hc by K T equals 56 times 1.931 times 6.626 times 10n to the power - 34 times speed of light that is 10 to power 10 to the power 10 and we have KT that is 1.381 times 10 to the power - -23 times T that is 298 and this value comes as 0.5223, so n 7 by n 0 is 8.90, so this is the ratio of the highest population to the population of J equals 0.

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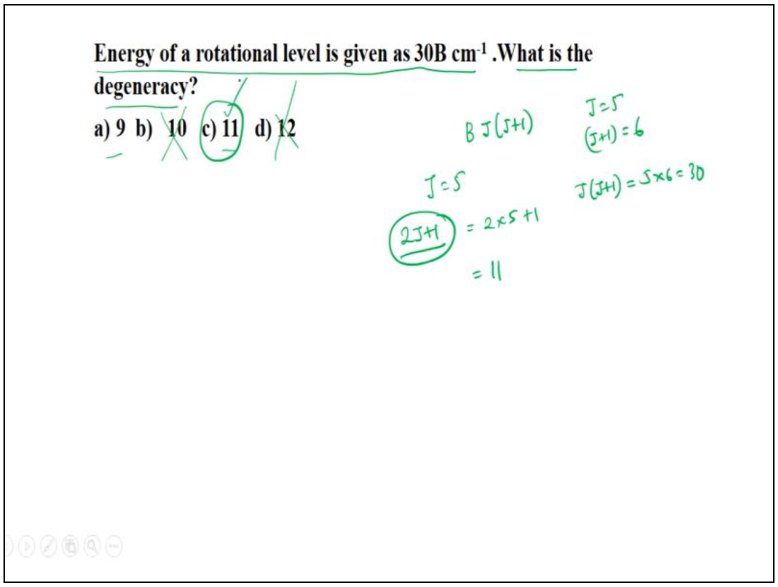

So, we have another question so this is a multiple choice question energy of a rotation on level is given as 30 B wave numbers. So, we have to find the degeneracy. So, the energy is given by B times J times J + 1, so we know if J equals 5 then J + 1 we can write as 6 and then J times J + 1 becomes 5 times 6 equals 30. So, we can easily find out here the value of J equals 5 so the degeneracy is 2 J + 1 that is 2 times 5 + 1 that is 11. So, the answer is C and because the degeneracy is always 2 J + 1 this is an odd number we know that 10 and 12 cannot be the answers.

So the answers could either be 9 and 11 and once we do the calculation we found the answer to be 11.

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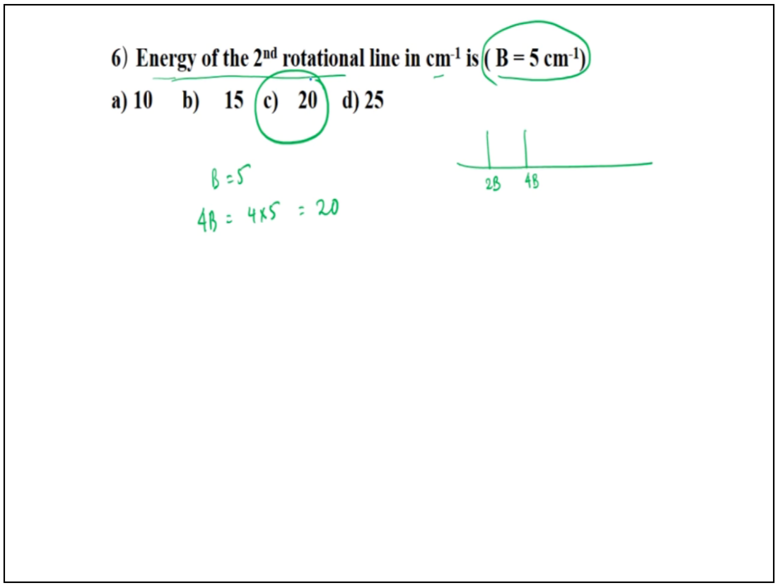

So there is another question that is the energy of the second rotation online in wave numbers, so what is given is B equals 5 wave numbers. so, we have to find the energy of the second rotational line? So, if we look into our rotation of spectrum the first rotation and line is at 2B and the second rotational line is at 4B and here B equals 5. So, 4 B equals 4 times 5 that is 20, so here we see that the correct answer is C that is 20 .